ON THE MIESCHER-BAER EMISSION BANDS IN THE FAR ULTRAVIOLET REGION[†]

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In studying a high-current discharge (of He + enriched $N^{15}O$ or ordinary NO), Miescher and Baer[1] found a new system of bands in the region from 1,368 to 1,680Å. These bands are single-headed and degraded toward the red. The vibrational frequency of the lower state is close to the frequency of the $X^1\Sigma_g^+$ state of the N_2 molecule as well as to that of the $A^2\Sigma^+$ state of the NO molecule. They did not find any alternation of intensity in the rotational structure, nor did they observe the heads of N_2^{15} isotope bands. Hence, they were unable to decide whether this system arose from the N_2 or the NO molecule.

With a view to determine experimentally the origin of these bands, we tried a high-current discharge of NO, (He + NO), N_2 and (He + N_2), each with and without a condenser. The 84-cm normal-incidence vacuum spectrograph was used.

We could not observe the bands in the condensed discharge of any of the above-mentioned gases, nor in the uncondensed discharges of N_2 and (He + N_2). We can, however, observe them in the uncondensed discharge of either pure NO or, much stronger, in the case of (He + NO). The results of the measurements are shown in Table I together with those of Miescher and Baer. In the present work, the system has been greatly extended towards shorter wavelengths, down to about 1,200Å. Some of the bands come close to and are confused with the Lyman-Birge-Hopfield bands of N_2, which appear quite strong in the region below 1,500Å. We can, nevertheless, discriminate between them by comparison with the picture of the pure N_2 spectrum because, as observed by Miescher and Baer, this new system has no intensity alternation in the rotational structure.

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[1]R. Miescher and P. Baer, Nature 169, 581 (1952).

TABLE I

v'	v''	ν observed (cm^{-1}) present	I	ν (cm^{-1}) Miescher and Baer
0	6	59513.9	1	59517
0	5	61702.5	2	61704
0	4	63908.8	4	63910
0	3	66149.4	6	66161
0	2	68431.3	6	68437
1	2	69988.3	5	69999
0	1	70745.4	5	70751
1	1	72307.6	6	72310
6	4	72585.8	1	
0	0	73083.9	3	73087
2	1	73819.8	3	
7	4	73874.9	1	
1	0	74642.5	5	
2	0	76158.0	5	
6	2	77121.8	1	
3	0	77636.1	6	
5	1	78134.2	1	
7	2	78361.9	4	
9	3			
4	0	79072.0	6	
6	1	79455.9	4	
5	0?	80488.1	1	
9	2	80645.2	2	$\omega_e' = 1599.6 cm^{-1}$
7	1	80690.1	1	
6	0	81768.8	3	$\omega_e'\chi_e' = 20.6 cm^{-1}$
8	1	81887.3	0	
7	0	83042.0	2	$\omega_e'' = 2366.5 cm^{-1}$
8	0	84209.8	2	
9	0	85284.9	1	$\omega_e''\chi_e'' = 14.6 cm^{-1}$
10	0	86214.3	1	

It seems probable that this system is due to NO or NO^+ rather than N_2. The reasons for this conclusion are the following. First of all, no intensity alternation is observed. Secondly, as pointed out by Miescher and Baer, there are no corresponding isotope bands of N_2^{15} observed. This new system appears only in the silent discharge of (He + NO) or NO and are not observed in the N_2 or (He + N_2) spectra. If we assume that the lower state of this system is $A^2\Sigma^+$ of NO, then the upper state is about 14.54eV above the v = 0 level of the ground state ($X^2\Pi$) of NO. Tanaka[2] has found several progressions of absorption bands in this region but none fit with the upper state of the present bands.

There is the possibility that this system is due to the NO^+ ion. As Mulliken[3] has pointed out, the ground state of NO^+ is $^1\Sigma^+$, having the electron configuration

[2] Y. Tanaka, Sci. Pap. Inst. Phys. Chem. Res., Tokyo 39, 456 (1942).

[3] R. S. Mulliken, Rev. Mod. Phys. 4, 73 (1932).

(kk) $\sigma^2\sigma^2\pi^4\sigma^2$, and both the dissociation energy and the vibration frequency of this state will be larger than that of the ground state of NO because the outermost antibonding electron $v\pi$ of the NO is missing in NO^+. We may then also expect a $^1\Pi$ excited state in NO^+ analogous to the upper state of the L-B-H bands of N_2 which falls at about 8.55eV from the ground state ($^1\Sigma_g^+$). The (0,0) band of the new system is 9.06eV, and both the ω_e' and ω_e'' values of this system agree closely with those of the $^1\Pi_g - ^1\Sigma_g^+$ system of N_2. Therefore, it seems quite probable that this system is due to transitions from the upper $^1\Pi$ state to the ground $^1\Sigma^+$ state of NO^+. Experimentally, this system appears far stronger in the case of (He + NO) compared with pure NO. This also seems to support the idea suggested above.

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